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3d and 4d Coordination Complexes and Coordination Polymers Involving Electroactive Tetrathiafulvalene Containing Ligands

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Abstract

The “through bond” approach has been recently developed to increase the interaction between the mobile π and localized d electrons in multifunctional molecular materials involving tetrathiafulvalene-based ligands. This paper reviews the 3d and 4d coordination complexes and polymers elaborated from a library of tetrathiafulvalene derivatives containing ligands obtained recently in our group. The different synthetic ways of the complexes are highlighted as well as their chemical and physical properties.

1. Introduction

Intense investigations are devoted to multifunctional molecular materials. Chemists and physicists are attracted to design new molecules and materials which possess synergy or interplay between two or more physical properties such as electrical conductivity, magnetic interactions, luminescence, light, chirality, etc... [1-9]. For the particular class of compounds involving electrical conductivity and magnetism, the objective is to establish a coupling between mobile electrons (π) and localized electrons (d). In molecular-based materials conduction electrons mainly arise from organic moieties assembled in networks while the spins mainly arise from transition metal ions. The strategy is to assemble these moieties with supramolecular chemistry tools. Two approaches are developed: a) A through-space approach, the interaction between mobile and localized electrons takes place through short contacts between chemical units, which usually lead weak interactions [10-17] b) A covalent approach, the interaction between localized and mobile electrons takes place through covalent

bonds. Whereas the first strategy leads to very weak π - d interactions, the second approach appears as a promising alternative to obtain strong π - d interactions and a large number of coordination complexes employing this approach have been studied [18-51]. In the later case, two procedures are used to prepare such materials: (i) a “one-pot” procedure which consists in a galvanostatic or chemical oxidation from the starting metal salts and neutral donor moieties, and (ii) a “step by step” procedure which consists in the synthesis of a paramagnetic transition-metal-based coordination complex involving neutral TTF derivatives, followed by a galvanostatic or chemical oxidation. However, only few of them have been successfully oxidized as radical cation complexes [52-57]. In order to realize the coordination of the $3d$ metal ions, a great variety of coordinating acceptors have been used such as amino, nitrilo, phenolate, phosphino, β -diketonate, pyrazine, pyrimidine, pyridine, pyridine- N -oxide, bipyridine groups.

Following the “through bond” approach, our group published in 2001 and 2003 one of the first Cu(II) coordination complex involving a TTF derivative as ligand [34] and its partially oxidized analogue [54], respectively. In this paper, we review the $3d$ and $4d$ coordination complexes obtained recently in our group using this approach (Fig. 1). The different and rational synthetic way to design mono-, di-, tri-nuclear and polymeric compounds are presented as well as their physical properties.

Ligands		Compounds		References
	L¹	$[M(hfac)_2(L^1)_2]$ M(II) = Mn, Cu and Zn	(1), (2) and (3)	[40]
	L²	$[Cu(hfac)_2(L^2)] \cdot H_2O$	(4)	[61]
	L³	$[Mn(hfac)_2(L^3)_2] \cdot (THF)_2$	(5)	[61]
	L⁴	$[Cu(hfac)_2(L^4)_2]$	(6)	[61]
	L⁵	$[Cu(hfac)_2(L^5)_2]$	(7)	[61]
	L⁶	$[M(hfac)_2(L^6)_2]$ M(II) = Mn, Cu and Zn	(8), (9) and (10)	[61]
	L⁷	$[Ru(salen)(PPh_3)(L^7)](BF_4)$ $[Cu_2(LH_2)(L^7)(H_2O)](ClO_4)_2 \cdot 1.5(H_2O)$ $[Co_2M(PhCOO)_6(L^7)_2] \cdot 2(CH_3CN)$ M(II) = Mn and Co	(11) (12) (15) and (16)	[41] [64] [39]
	L⁸	$[Cu_2(L^8)_2]$	(13)	[66]
	L⁹	$[Co_2(PhCOO)_4(L^9)_2]$	(14)	[68]
	L¹⁰	$[M(L^{10})_2M(H_2O)_4](XO)_2 \cdot 2(H_2O)$ M(II) = Mn, Co, Zn and Cd, X = BF_4^- and ClO_4^-	(17)-(20)	[76]

Fig. 1. Functionalized ligands and related coordination complexes.

2. Mononuclear Complexes

The first imine-bridged pyridyltetrathiafulvalene building block has been synthesized via the Schiff base condensation of formyltetrathiafulvalene and 2-aminopyridine [43]. Using this synthetic method, the tetrathiafulvalene-imino-2-pyrazine ligand **L¹** was synthesized [40]. Its coordination reaction with the $[M(hfac)_2] \cdot xH_2O$ precursors led to two families of molecular complexes [40]: *Cis*- $[M(hfac)_2(L^1)_2]$ (**1**) (Fig. 2a) and *Trans*- $[M(hfac)_2(L^1)_2]$ (Fig. 2b) (M = Cu (**2**), Zn (**3**)) in which two organic ligands **L¹** were covalently linked through the delocalized π imine systems in *cis* or *trans* conformation. Efficient electronic communication between the imino-pyrazine systems and the TTF core was demonstrated by cyclic voltammetry experiments because the oxidation of complexes occurs at higher potentials than for the free ligand. The dissociation of **1** in solution was observed by kinetic electrochemical measurements while **2** and **3** do not dissociate attesting the stability of the *trans* conformation compared to the *cis*.

The amido bridge is a famous chemical linker to assemble the TTF core and the

coordinating acceptor because of its ability to interact with neighbours through hydrogen bonds. This fact comes from the H-bond acceptor (carbonyl group) and H-bond donor (amido group). The most studied TTF-based ligands involving such bridge are based on the ethylenedithio-TTF (EDT-TTF) and bithiomethyl-TTF (BTM-TTF) [23] [58-60]. Our objective was to use the amido bridge due to its easy chemical procedure to link the TTF core to divers acceptor moieties. With this mind, we designed a library of amido-TTF ligands with 2-pyrimidine (**L**²), 4-pyridine (**L**³), 2-pyrazine (**L**⁴), 2-pyridine (**L**⁵) and 2-pyridine-N-oxide (**L**⁶) (Fig. 1) [61]. All these ligands were used to synthesize 3d transition-metal-based mononuclear coordination complexes (Fig. 2). For **L**², a 1:1 complex of penta-coordinated Cu(II) is obtained (Cu(hfac)₂(**L**²)]·H₂O (**4**) (Fig. 2c) while for the **L**²-**L**⁶ ligands, 1:2 complexes **5-10** are isolated (Fig.2 d-g).

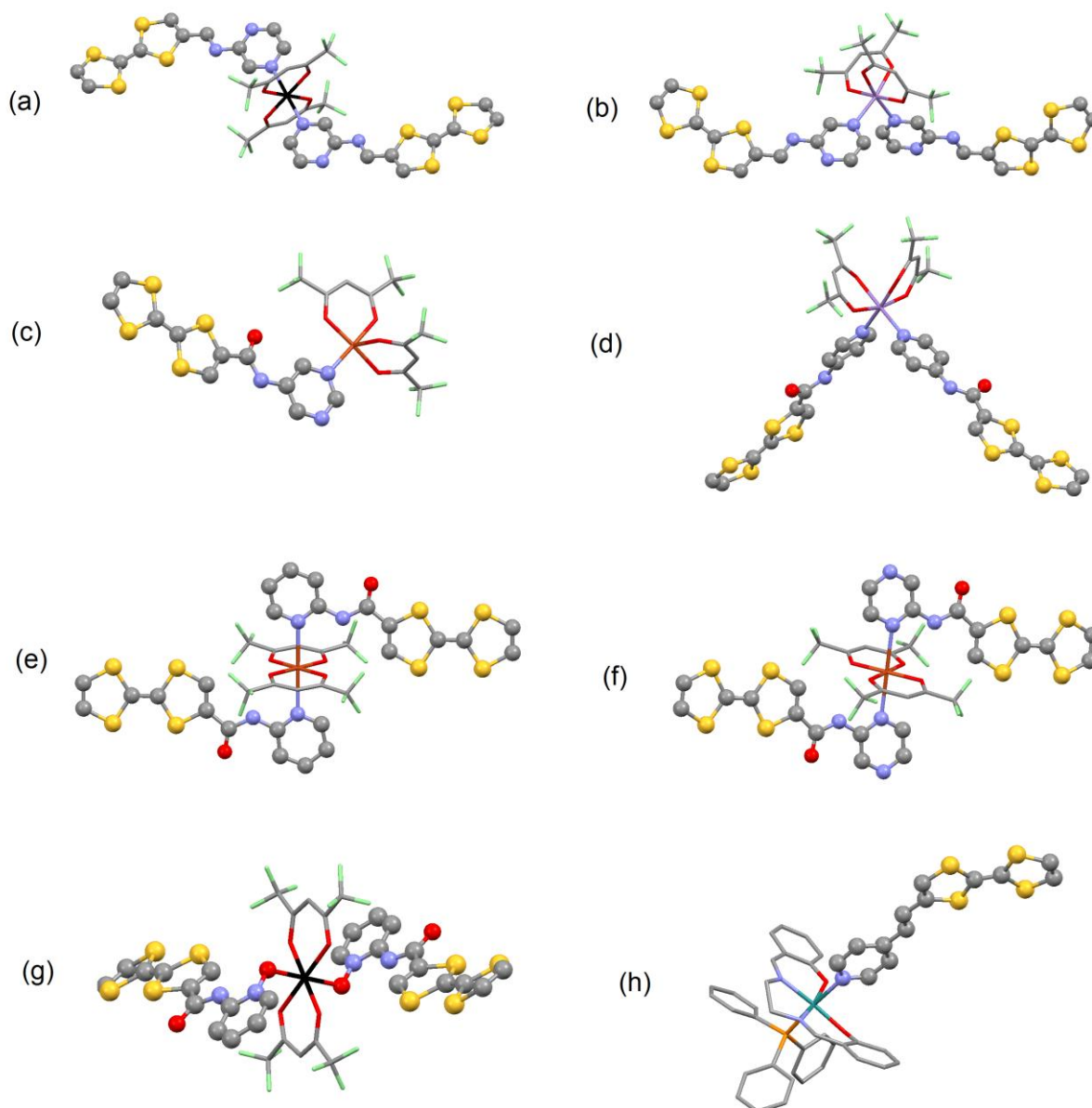


Fig. 2. *3d* (a-g) and *4d* (h) mononuclear complexes involving electroactive functionalized TTF ligands. (a) stands for (2) and (3), (b) for (1), (c) for (4), (d) for (5), (e) for (7), (f) for (6), (g) for (8) to (10) and (h) for (11) complexes.

The cyclic voltametry of the ligands and related complexes present two reversible monoelectronic oxidations at 0.50 and 0.90 V vs SCE attributed to the formation of radical cation and dication species. The coordination effect of the $M(hfac)_2$ units is not evaluable using this technique since no significant shift of the oxidation potentials is observed. To realize such a study, all the compounds were investigated by solid-state UV-visible absorption spectroscopy. In this review, the discussion focus on the two compounds 7 and 9. The experimental curves are fitted by Gaussian deconvolutions and the absorption bands assigned

by Time-Dependent Density Functional Theory (TD-DFT) calculations (Fig. 3) [61].

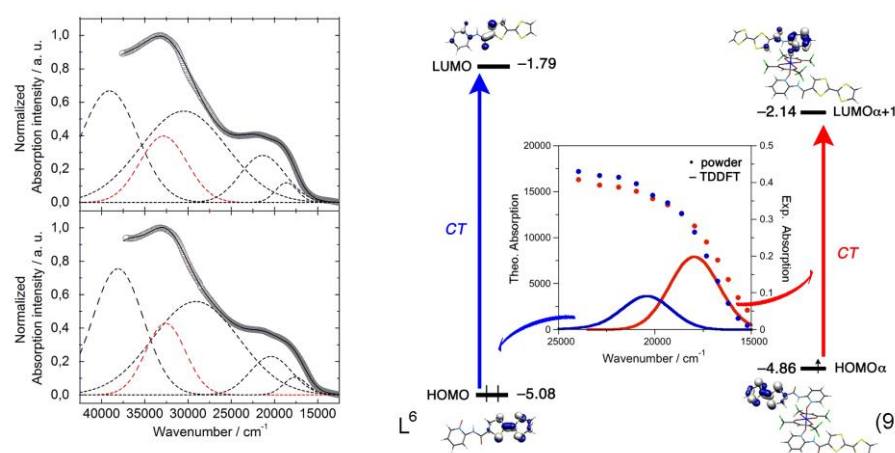


Fig. 3. (Left part) Experimental solid state UV-visible absorption spectra for complexes **7** and **9** (open gray circles). Gaussian deconvolutions of the experimental curves are shown in dashed lines and the best fit in full black lines, $R = 0.9996$ and 0.9999 respectively for **7** and **9**. (Right part) Energy stabilisation of the HOMO \rightarrow LUMO charge transfer after coordination.

The low energy transitions are identified as mono-electronic HOMO \rightarrow LUMO charge transfers (CTs) from TTF donor fragment to acceptor moiety (Fig. 3), whereas the high-energy region is composed of π - π^* intraligand excitations. The CTs are red-shifted in the coordination complexes compared to the free ligands by a value of 2500 cm^{-1} for **9** (Fig. 3) while the energy-shift is weaker in **7** with a value of 1500 cm^{-1} . To interpret this result it was demonstrated that, i) the coordination effect is electrostatic since the CT bands are not shifted in the isostructural complexes **8-10**, ii) the small coordination effect in **7** is due to the orientation of the Jahn-Teller axis along the O-Cu-O direction while it is in the plane formed by the hfac^- anions for **9** [61].

Ten years ago, our group published one of the first coordinated Cu(II) complex involving the 4-(2-tetrathiafulvalenylethenyl)pyridine ligand (**L**⁷) (Fig. 1) [34]. Later it was demonstrated that the **L**⁷ ligand can be partially [54] or fully [53] oxidized when it is coordinated to a 3d transition metal. In 2008, this same ligand permitted to publish the first paramagnetic coordination complex based on the 4d Ru(III) ion [41]. This work was motivated by the more radially extended valence 4d orbitals compared with their 3d analogues. Thus, from a magnetic point of view, an enhancement of the exchange interaction might be expected between interacting magnetic centres [62]. The 4d complex of formula

[Ru(salen)(PPh₃)(L⁷)]BF₄ (**11**) (with salen = N,N'-ethan-1,2-diylbis(salicylideneamine) and PPh₃ = triphenylphosphine) displayed remarkable electrochemistry (Fig. 4) [41]. In fact, four reversible single-electron oxidation waves were observed corresponding to the formation of a Ru(III), TTF radical cation, TTF dication and Ru(IV) species respectively. The oxidation potentials are anodically shifted with respect to the potentials measured for the [Ru(salen)(PPh₃)(Cl)] precursor and free L⁷ ligand due to the electron-withdrawing of L⁷ and coordination of the Ru(III) metallic precursor. **11** is an adequate molecular precursor for 4*d* paramagnetic conducting material since the oxidation waves of L⁷ are measured at lower potentials than the one for the oxidation of Ru(III) in diamagnetic Ru(IV). The confirmation of the Ru(III) (*S* = ½) centred paramagnetism of **11** is given by the three-line EPR spectrum which is simulated with *g*₁=2.28, *g*₂=2.12 and *g*₃=1.92 (Fig. 4) [41] [63].

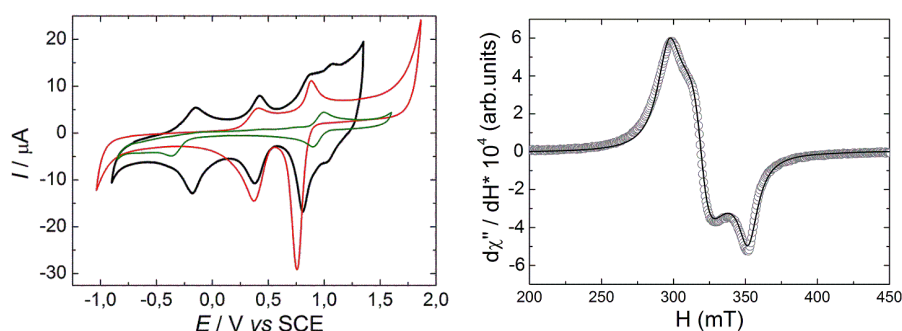


Fig. 4. (Left part) Cyclic voltammetry of **11** (full black line), L⁷ (full red line) and precursor [Ru(salen)(PPh₃)(Cl)] (full green line) in CH₂Cl₂ at a scan rate of 100 mV.s⁻¹. (right part) Experimental X-band (9.470 GHz) EPR spectrum of a powder sample of **11** at 67 K (gray circles) and its best simulation (full blackline).

3. Dinuclear Complexes

Few synthetic strategies can be explored to increase the nuclearity of the molecular edifices. The first approach towards conducting materials based on TTF ligands consists of the polynuclear complex functionalisation.

Following this way, the Cu(II) dimer [Cu₂(LH)₂(H₂O)₂]²⁺ (**12**) (LH₂ = 1:2 Schiff base of 1,3-diaminobenzene and butanedione monoxime) (Fig. 5a) was decorated by one L⁷ ligand [64]. **12** is composed of two Cu(II) centres coordinated to two Schiff base ligands constituting the base of the square-pyramidal prism. The L⁷ donor occupies the axial position of one of the Cu(II) while the axial position of the other Cu(II) ion is filled by a water molecule.

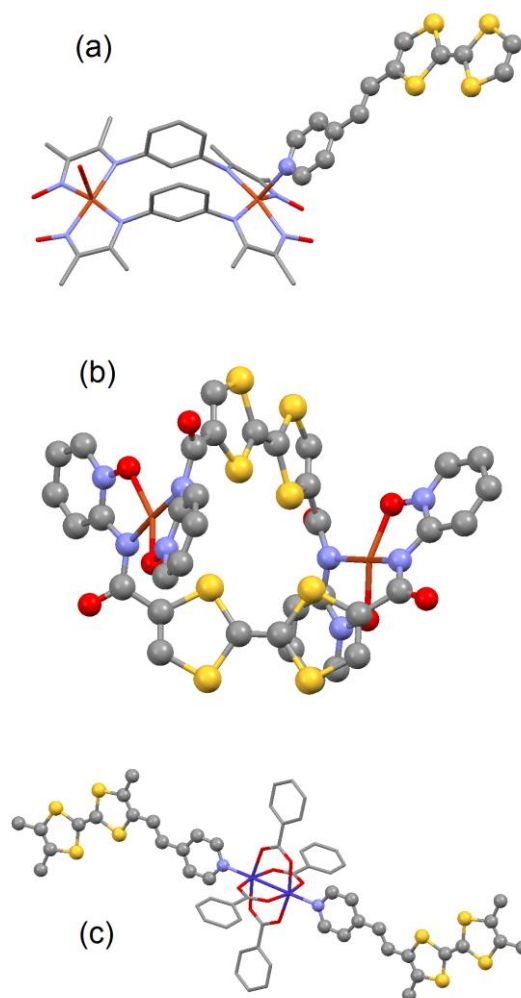


Fig. 5. Dinuclear complexes involving electroactive functionalized TTF ligands. (a) stands for complex (**12**), (b) for (**13**) and (c) for (**14**).

The meta substitution of the benzene ring allows exciting ferromagnetic interactions as calculated using slightly modified Bleaney-Bowers model with Hamiltonian $H = -JS_1S_2$ [65], and interdimer coupling zJ' (Fig. 6). The best result gave a ferromagnetic interaction ($J = 10.90(7) \text{ cm}^{-1}$, $zJ' = 0.290(2) \text{ cm}^{-1}$ and $g = 2.072(1)$) between the two Cu(II) through the Schiff base. This interaction is obviously not due to the presence of the L^7 ligand but demonstrates that the functionalisation does not suppress the intrinsic properties of the metallic precursor.

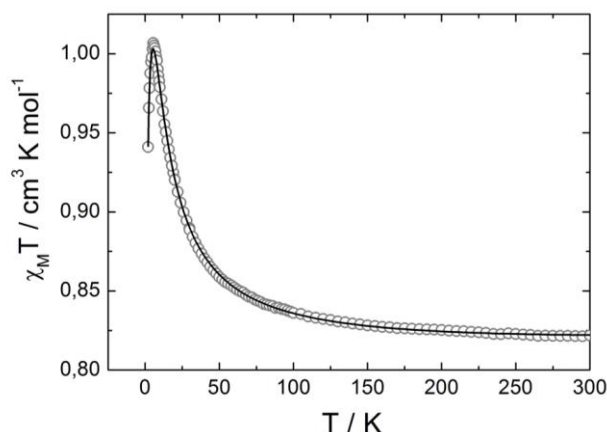


Fig. 6. Thermal variation of the $\chi_M T$ product with the best fit for **12**.

The second strategy consists of the multifunctionality of the TTF core. Thus the TTF core was substituted by two amido-2-pyridine-*N*-oxide acceptors following the same synthetic strategy already given for **L**⁶ (cf paragraph 2) [66].

In the presence of the metallic precursor $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$, the resulting *cis* and *trans* mixture of the ligand **L**⁸ give the surprising dinuclear complex $[\text{Cu}_2(\text{L}^8)_2]$ (**13**) (Fig. 5b). It is worth noticing that only the *cis* isomer is involved in **13** and the hfac^- anions were not any more coordinated to the Cu(II) in order to compensate the deprotonation of the amido bridges. Both Cu(II) are coordinated to the pyridine-*N*-oxide and amido-bridge in a square planar geometry. The paramagnetism is due to the two Cu(II) centres and the $\chi_M T$ product is equal to $0.84 \text{ cm}^3 \text{ K mol}^{-1}$ with a spin density distribution localised in the square planes. The most interesting property in this complex is the electrochemical behaviour. The first oxidation wave is split due to the non equivalence of both donor and the rigidity of **13**. The splitting was attributed to the formation of mixed valence dimer [67]. The oxidation waves are cathodically shifted by a value of 0.1 V in the complex compared to the ones of the free ligand due to the deprotonation of the amido bridges. The experimental and theoretical (TD-DFT) photophysical properties clearly demonstrate that both deprotonation and coordination effects compensate themselves in **13** [67].

The last strategy consists of a synthesis protocol of two-steps one-pot reaction. The first step is the in situ generation of carboxylate anions via oxidation of aromatic aldehydes by metal nitrates in air [68]. The aldehydes act as solvents and are also involved in redox processes. Solutions containing solely transition metal cations and aromatic carboxylates are obtained following this procedure. The second step is the formation of the polynuclear

carboxylato complexes from solutions obtained at the former stage upon addition of different solvents. Thus, to a hot mixture of Co(II) salt and benzaldehyde, the addition of **L**⁹ in toluene led to the formation of the dinuclear complex of formula [Co₂(PhCOO)₄(**L**⁹)₂] (**14**) (Fig. 5c) [69]. The X-ray structure is composed of a well known paddlewheel structure core Co₂(PhCOO)₄ with a Co-Co distance equal to 2.772(2) Å, which is in the range of metal-metal distances measured in other Co₂(RCOO)₄ complexes [70]. The coordination sphere of each Co(II) centers is filled by one **L**⁹ apical ligand. The magnetic analysis gives antiferromagnetic exchange interaction between the Co(II) ions ($J = -420 \text{ cm}^{-1}$ and $g = 4.78$). In the Co(II)-based complex, structural and magnetic data highlight weak metal-metal interactions. The antiferromagnetic behaviour is explained as the result of the direct exchange between metal centres. This complex was the first Co(II) dimer complex with a paddlewheel structure and having strong electron donors as an apical ligand.

4. Trinuclear complex

In 2007, our team published the first homo- and hetero-trinuclear TTF-based complex with the **L**⁷ ligand (Fig. 1) [39]. The compounds of formula [Co₂M(PhCOO)₆(**L**⁷)₂]·2(CH₃CN) (M(II) = Mn (**15**) and Co (**16**)) were obtained using the strategy which has given the Co(II) paddlewheel structure **14**. The molecular structures of **15** and **16** consist of centrosymmetric trimetallic units, the three metal ions are bridged by benzoate ligands and the outer metal ions are coordinated by ligands **L**⁷ through the nitrogen atom of pyridyl (Fig. 7a). The octahedral coordination sphere of the central metal ion is made of six oxygen atoms coming from different benzoates and it is quite regular. The two peripheric cobalt ions lie in a distorted trigonal bipyramidal surrounding. The Co2...Co1 [Mn1] distance is equal to 3.5620(7) [3.6279(3)] Å. The bond lengths and bond angles of the TTF moiety are close to those reported for the non-coordinated neutral unit [34]-[38], indicating that **L**⁷ is neutral. The crystal structure packing pattern consists of an alternating arrangement of organic and inorganic layers.

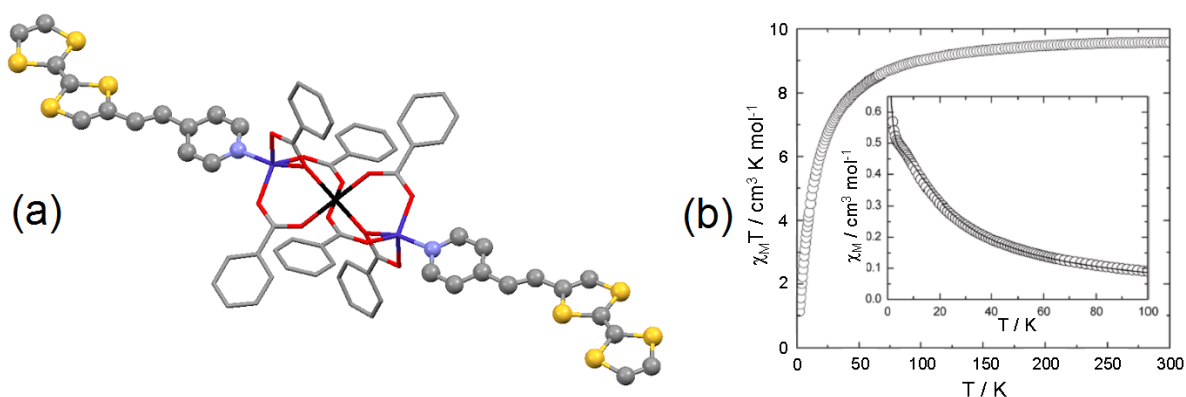


Fig. 7. (a) Molecular structure of the trinuclear complexes involving electroactive functionalized TTF ligands $[\text{Co}_2\text{M}(\text{PhCOO})_6(\text{L}^7)_2]$ $\text{M}(\text{II}) = \text{Mn}$ (**15**) and Co (**16**). The $\text{Co}(\text{II})$ and $\text{M}(\text{II})$ (Mn and Co) ions are in blue and black respectively. (b) Thermal variation of the magnetic susceptibility of **15**.

Compound **16** displays a room temperature $\chi_{\text{M}}T$ value of $8.56 \text{ cm}^3 \text{ K mol}^{-1}$ giving a calculated Zeeman factor of octahedral cobalt equal to 2.78. This value falls in the range of commonly accepted g values for octahedral $\text{Co}(\text{II})$, specially when the octahedral coordination sphere is just slightly distorted [71]. On cooling, $\chi_{\text{M}}T$ decreases and passes through a minimum, then increases until 2 K. The decreasing of $\chi_{\text{M}}T$ was attributed to three phenomena [72]: i) Spin-orbit coupling of the $\text{Co}(\text{II})$ ions, ii) distortions of the octahedral environment on $\text{Co}(\text{II})$ and iii) Antiferromagnetic superexchange interaction between central $\text{Co}(\text{II})$ ion and the two terminal five-coordinated $\text{Co}(\text{II})$ ions. The presence of the minimum is systematic but its amplitude is sample dependent and thus prevents any quantitative analysis.

For **15**, starting from the fact that the magnetic properties could be analyzed below 100 K considering a purely isotropic spin system [73] and only nearest neighbour superexchange interactions, a quantitative analysis could be realized using the following Hamiltonian: $H = -J S_{\text{Co}} \cdot S_{\text{Mn}} + g_{\text{Co}} \beta H \cdot S_{\text{Co}} + g_{\text{Mn}} \beta H \cdot S_{\text{Mn}}$ with $S_{\text{Co}} = S_{\text{Co1}} + S_{\text{Co2}}$ where Co1 and Co2 are the octahedral and trigonal bipyramidal Cobalt respectively. The zero-field magnetic susceptibility is obtained applying the simplified Van Vleck formula; i.e., without the second order Zeeman perturbation [71]. The best parameters are $g_{\text{Mn}} = 2.00$ and $g_{\text{Co}} = 2.29$ with antiferromagnetic interactions between the $\text{Mn}(\text{II})$ and $\text{Co}(\text{II})$ ions ($J = -1.80 \text{ cm}^{-1}$) (Fig. 7b).

5. Polymeric compounds

The last category of compounds, which is tackled in this article, concerns coordination

polymers involving oxidized TTF. Only few examples of such compounds with paramagnetic $3d$ ions are reported in the literature [74]–[76].

The polymeric compounds of formula $[M1(L^{10\bullet+})_2M2(H_2O)_4](X)_6 \cdot 2H_2O$, $M1(II)=M2(II)= Mn$ (**17**), Co (**18**), Zn (**19**) and Cd (**20**), $X = BF_4^-$ and ClO_4^- have been obtained by electrocrystallisation from the tetrathiolate 2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene ligand L^{10} (Fig. 1) [76]. They consist of oxidized TTF derivatives covalently linked to a $3d$ or $4d$ (for $Cd(II)$) transition metal as a result of a metal–nitrile interaction, which yields 2D networks (Fig. 8). The centrosymmetric coordination spheres of the two metals ions $M1$ and $M2$ are different. That of $M1$ is built up with six nitrogen atoms from four $L^{10\bullet+}$. The second metal ion $M2$ lies in a centrosymmetric octahedral coordination sphere built with four oxygen atoms $O1$ and $O2$ from water molecules and two $N1$ nitrogen atoms belonging to two $L^{10\bullet+}$. As a result of both centrosymmetry and translation, the $L^{10\bullet+}$ and $M1$ form infinite double $L^{10}/M1$ chains along the a axis (Fig. 8a). The second metal site $M2$ acts as a bridging unit between two double chains in the b direction to build a polymeric 2D network lying in the ab plane (Fig. 8b).

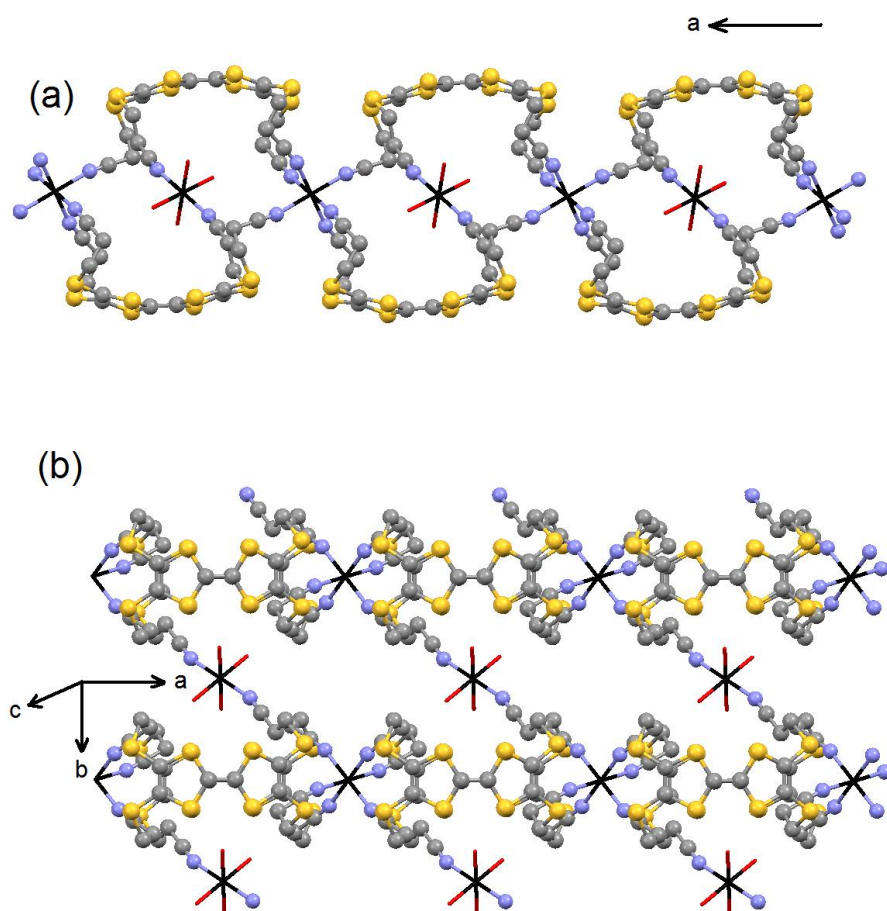


Fig. 8. Molecular structure of the bidimensional polymers involving electroactive functionalized TTF ligands $[M(L^{10})_2M(H_2O)_4](X)_6 \cdot 2(H_2O)$ $M(II) = Mn$ (**17**), Co (**18**), Zn (**19**) and Cd (**20**), $X = BF_4^-$ and ClO_4^- . (a) Double chains running along the a axis. (b) Polymeric 2D network lying in the ab plane.

Both polymers have a paramagnetic behaviour with a small magnetic contribution of the radical cations due to strong interactions between them. IR, Raman and UV/Vis absorption spectroscopy were performed to confirm the radical cation form of L^{10} : i) IR spectroscopy shows a shift of 50 cm^{-1} to lower frequencies of the C=C anti-symmetrical stretching, ii) Raman spectroscopy shows a shift of 100 cm^{-1} to lower frequencies of the C=C symmetrical stretching. These results are in agreement with the oxidation effects observed for the TTF and tetra-methyl-TTF (TMTTF) [77]. iii) A strong absorption band centred at 14000 cm^{-1} was observed and attributed to SOMO-n \rightarrow SOMO charge transfer from the 2-cyanoethylthio arms to the TTF radical cationic core (where SOMO-n is an orbital lower in energy than the SOMO) [78]. The full oxidation of the donors led to a semi-conductor behaviour with a room temperature resistivity equal to $4 \times 10^4\ \Omega\text{ cm}$.

6. Conclusions

A library of TTF-based ligands has been synthesized. They involved several acceptors like pyridine, pyrimidine, pyrazine, pyridine-*N*-oxide and nitrile moieties which are coordinated to the TTF core via a chemical bridge such as imine, amide, ethylenyl...

The simple reactions with the metallic precursors $M(hfac)_2 \cdot xH_2O$ led to ten new mononuclear complexes. The cyclic voltametry attested the electro-activity of the compounds. The coordination effects have been evaluated from the UV-visible absorption spectroscopy in experimental and theoretical (TD-DFT) points of view. The first $4d$ paramagnetic complex with a TTF-based ligand (L^7) was obtained from a Ru(III) Schiff base precursor. It was demonstrated that the paramagnetism came from the Ru(III) ion and that both metal center and L^7 could be reversibly oxidized and reduced.

In order to increase the nuclearity of the complexes, i.e. to obtain di- and tri-nuclear complexes, three synthetic ways have been reported: i) the functionalization with TTF ligands of polynuclear metallic precursors. Using this strategy a dinuclear of Cu(II) in which ferromagnetic interactions take place, was obtained. ii) The TTF core is multi-functionalized

to increase the number of coordination sites. This strategy was used to study a dinuclear complex of Cu(II) that may form a mixed valence dimer. iii) The last strategy consists of the in situ generation of carboxylate anions via oxidation of aromatic aldehydes followed by the coordination of the apical TTF ligands. The first homo and hetero bi- and tri-nuclear complexes were obtained. Quantitative magnetic investigations of the systems were performed and they can be described as antiferro- and ferri-magnetic systems.

Finally the tetra-functionalization of the TTF core with nitrilo arms and the synthetic protocol of electro-crystallization led to the formation of bi-dimensional networks which present paramagnetic and semi-conducting behaviours.

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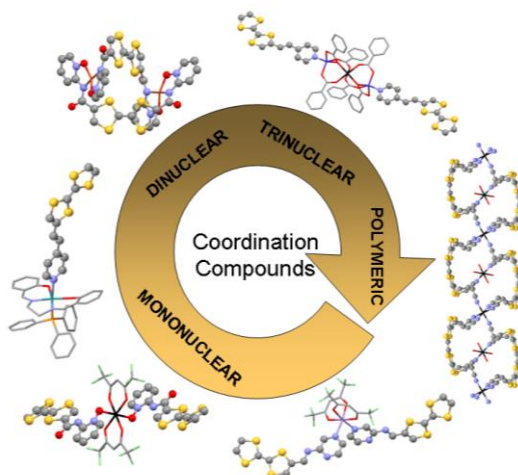
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A library of tetrathiafulvalene ligands was elaborated and used in different synthetic ways in order to design mono-, di-, tri-nuclear and polymeric coordination compounds. They display electrochemical, magnetic and photo-physical properties that make them good candidates for future multifunctional conducting materials.